



European Patent Office.

1
 2
 3
 4
 5
 6
 7
 8
 9
 10
 11
 12
 13
 14
 15
 16
 17
 18
 19
 20
 21
 22
 23
 24
 25
 26
 27
 28
 29
 30
 31
 32
 33
 34
 35
 36
 37
 38
 39
 40
 41
 42
 43
 44
 45
 46
 47
 48
 49
 50
 51
 52
 53
 54
 55
 56
 57
 58
 59
 60
 61
 62
 63
 64
 65
 66
 67
 68
 69
 70
 71
 72
 73
 74
 75
 76
 77
 78
 79
 80
 81
 82
 83
 84
 85
 86
 87
 88
 89
 90
 91
 92
 93
 94
 95
 96
 97
 98
 99
 100
 101
 102
 103
 104
 105
 106
 107
 108
 109
 110
 111
 112
 113
 114
 115
 116
 117
 118
 119
 120
 121
 122
 123
 124
 125
 126
 127
 128
 129
 130
 131
 132
 133
 134
 135
 136
 137
 138
 139
 140
 141
 142
 143
 144
 145
 146
 147
 148
 149
 150
 151
 152
 153
 154
 155
 156
 157
 158
 159
 160
 161
 162
 163
 164
 165
 166
 167
 168
 169
 170
 171
 172
 173
 174
 175
 176
 177
 178
 179
 180
 181
 182
 183
 184
 185
 186
 187
 188
 189
 190
 191
 192
 193
 194
 195
 196
 197
 198
 199
 200
 201
 202
 203
 204
 205
 206
 207
 208
 209
 210
 211
 212
 213
 214
 215
 216
 217
 218
 219
 220
 221
 222
 223
 224
 225
 226
 227
 228
 229
 230
 231
 232
 233
 234
 235
 236
 237
 238
 239
 240
 241
 242
 243
 244
 245
 246
 247
 248
 249
 250
 251
 252
 253
 254
 255
 256
 257
 258
 259
 260
 261
 262
 263
 264
 265
 266
 267
 268
 269
 270
 271
 272
 273
 274
 275
 276
 277
 278
 279
 280
 281
 282
 283
 284
 285
 286
 287
 288
 289
 290
 291
 292
 293
 294
 295
 296
 297
 298
 299
 300
 301
 302
 303
 304
 305
 306
 307
 308
 309
 310
 311
 312
 313
 314
 315
 316
 317
 318
 319
 320
 321
 322
 323
 324
 325
 326
 327
 328
 329
 330
 331
 332
 333
 334
 335
 336
 337
 338
 339
 340
 341
 342
 343
 344
 345
 346
 347
 348
 349
 350
 351
 352
 353
 354
 355
 356
 357
 358
 359
 360
 361
 362
 363
 364
 365
 366
 367
 368
 369
 370
 371
 372
 373
 374
 375
 376
 377
 378
 379
 380
 381
 382
 383
 384
 385
 386
 387
 388
 389
 390
 391
 392
 393
 394
 395
 396
 397
 398
 399
 400
 401
 402
 403
 404
 405
 406
 407
 408
 409
 410
 411
 412
 413
 414
 415
 416
 417
 418
 419
 420
 421
 422
 423
 424
 425
 426
 427
 428
 429
 430
 431
 432
 433
 434
 435
 436
 437
 438
 439
 440
 441
 442
 443
 444
 445
 446
 447
 448
 449
 450
 451
 452
 453
 454
 455
 456
 457
 458
 459
 460
 461
 462
 463
 464
 465
 466
 467
 468
 469
 470
 471
 472
 473
 474
 475
 476
 477
 478
 479
 480
 481
 482
 483
 484
 485
 486
 487
 488
 489
 490
 491
 492
 493
 494
 495
 496
 497
 498
 499
 500
 501
 502
 503
 504
 505
 506
 507
 508
 509
 510
 511
 512
 513
 514
 515
 516
 517
 518
 519
 520
 521
 522
 523
 524
 525

(11)

EP 0 810 666 A1

(12)

EUROPEAN PATENT APPLICATION

(51) Int. Cl.⁶: **H01L 27/115**

(21) Application number: 97108107.0

(22) Date of filing: 16.05.1997

(72) Inventor: Yamanobe, Tomomi
7-12, Toranomon 1-chome, Minato-ku Tokyo (JP)

(30) Priority: 30.05.1996 JP 137245/96

(74) Representative:
Herrmann-Trentepohl, Werner, Dipl.-Ing.
Patentanwälte
Herrmann-Trentepohl
Grosse - Bockhorni & Partner
Forstenrieder Allee 59
81476 München (DE)

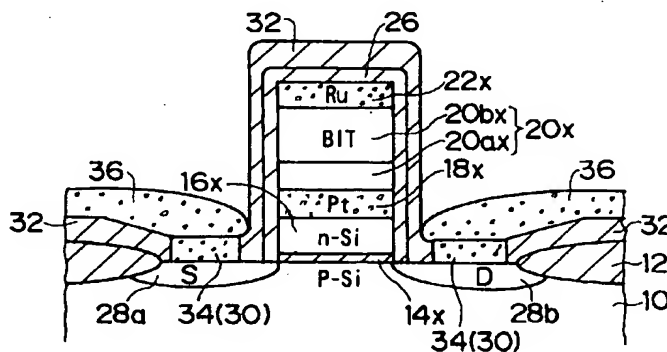
(71) Applicant:
Oki Electric Industry Co., Ltd.
Tokyo (JP)

(54) Non-volatile semiconductor memory cell and method for production thereof

(57) A non-volatile semiconductor memory cell employing a field effect transistor having a gate of the metal/ferroelectric structure or the metal / ferroelectric /metal / insulator structure, wherein the ferroelectric layer is a layer of bismuth titanate containing bismuth more than the stoichiometric quantity or a piled layer of bismuth titanate of the stoichiometric composition and

bismuth titanate containing bismuth more than the stoichiometric quantity, both of which have a less amount of dielectric constant and remanent polarization, thereby enabling the non-volatile memory cell to memorize and erase binary information with a less amount of voltage to be applied to the gate.

FIG. 4 (C)



Description

TECHNICAL FIELD

This invention relates to a non-volatile semiconductor memory cell under the category of a single transistor memory cell employing a field effect transistor having a ferroelectric layer as the gate insulator thereof and a method for producing the non-volatile semiconductor memory cell.

BACKGROUND OF THE INVENTION

A non-volatile semiconductor memory cell which employs a field effect transistor which further employs a ferroelectric material, such as lead zirconate titanate ($\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$) and bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$), as the material for the gate insulator layer, is available in the prior art. The field effect transistor has a metal-ferroelectric-semiconductor (MFS) structure. Since a ferroelectric material has a large amount of remanent polarization, a field effect transistor having a gate insulator of a ferroelectric material has a memory function. In other words, once a positive voltage is applied to the gate electrode of an n-channel metal-ferroelectric-semiconductor (MFS) field effect transistor, polarization remains in the gate insulator made of a ferroelectric material even after the voltage is removed, due to the phenomenon of remanent polarization. As a result, an n-channel is memorized along the surface of the semiconductor layer. The memorized n-channel can readily be read out by applying a voltage across the n-channel or between a source and a drain. The memorized information can readily be erased by application of a negative voltage to the gate electrode of the n-channel MFS field effect transistor. When the MFS field effect transistor is a p-channel transistor, the polarity of the voltage to be applied to the gate electrode of the field effect transistor should be reversed to a negative voltage. In this manner, binary information which can be represented by existence or non-existence of a drain current flowing in the MFS field effect transistor can be memorized in an MFS field effect transistor.

Since an MFS field effect transistor is involved with some problems, e.g. the difficulty of depositing a ferroelectric layer directly on a silicon substrate, formation of an unnecessary silicon dioxide layer during a thermal treatment and the like, however, a metal-ferroelectric-metal-insulator-semiconductor (MF MIS) field effect transistor was developed (ISSCC 95 February 1995 A Single-Transistor Ferroelectric Memory Cell T. Nakamura et al.).

The gate of a metal-ferroelectric-metal-insulator-semiconductor (MF MIS) field effect transistor is a series circuit of 2 capacitors including an upper capacitor consisting of an upper metal layer, a ferroelectric layer and a lower metal layer, and a lower capacitor consisting of the lower metal layer, an insulator layer and a semiconductor layer. The voltage applied to the gate is divided

into two including the first voltage portion applied to the upper capacitor and the second voltage portion applied to the lower capacitor. Since the dielectric constant of a ferroelectric material is much larger than that of the ordinary insulator e.g. silicon dioxide, the capacity of the upper capacitor is much larger than that of the lower capacitor, resulting in a less amount of the first voltage portion and a larger amount of the second voltage portion. As a result, the intensity of the electric field becomes less in the ferroelectric layer, resulting in a less magnitude of remanent polarization in the ferroelectric layer. This causes malfunction for the non-volatile semiconductor memory cell.

An attempt to make the remanent polarization in the ferroelectric layer sufficiently large, is resultantly accompanied by a requirement to make the voltage to be applied to the second capacitor larger. As a result, the amount of the voltage to be applied between the gate electrode and the semiconductor layer or substrate is required to be larger. This causes a possibility of breakdown of the lower capacitor.

In conclusion, a non-volatile semiconductor memory cell employing a MF MIS field effect transistor is involved with a drawback in which a higher voltage is required for writing information therein.

OBJECTS AND SUMMARY OF THE INVENTION

An object of this invention is to provide a non-volatile semiconductor memory cell employing an MFS or MF MIS field effect transistor which allows a less amount of voltage to be applied between the gate electrode and the semiconductor substrate, to write a piece of binary information therein.

The other object of this invention is to provide a method for producing a non-volatile semiconductor memory cell employing an MFS or MF MIS field effect transistor which allows a less amount of the voltage to be applied between the gate electrode and the semiconductor substrate, to write a piece of binary information therein.

This invention is based on the concept tabulated below :

1. A dielectric material having a less amount of dielectric constant produces a capacitor having a less amount of capacity, when it is employed as the dielectric layer of the capacitor. A capacitor having a less amount of the capacity causes a larger amount of the voltage allotted to the capacitor, when it is connected in series with the other capacitor. Therefore, a layer of a ferroelectric material having a less amount of dielectric constant is effective to allot a larger amount of voltage to the upper capacitor, resultantly causing a larger amount of intensity of electric field in the ferroelectric layer of the upper capacitor with a less amount of voltage to be applied between the gate electrode and the semiconductor substrate.

2. A less amount of remanent polarization is effective to increase the intensity of electric field in the ferroelectric layer.

3. A layer of bismuth titanate containing bismuth more than the stoichiometric quantity, in which the direction of the c-axis is perpendicular to the surface of the bismuth titanate layer, has a less amount of dielectric constant and remanent polarization than a layer of bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) of the stoichiometric composition.

4. A layer of bismuth titanate of the stoichiometric composition produced on a layer of bismuth titanate containing bismuth more than the stoichiometric quantity, in which the direction of the c-axis is perpendicular to the surface of the bismuth titanate layer, has a less amount of dielectric constant and remanent polarization than a layer of bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) of the stoichiometric composition.

5. A layer of bismuth titanate of the stoichiometric composition produced on a layer of bismuth titanate containing bismuth more than the stoichiometric quantity, has a flat top surface.

6. A layer of bismuth titanate containing bismuth more than the stoichiometric quantity can be produced on a substrate by spin coating an organic solvent solution containing a bismuth source and a titanium source at a mole ratio at which bismuth component is more than 4 and the titanium component is 3, on the substrate and applying a thermal treatment process for drying and crystallizing the spin coated film.

7. A layer of bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) of the stoichiometric composition can be produced on a substrate by spin coating an organic solvent solution containing a bismuth source and a titanium source at a mole ratio of 4 : 3 and applying a thermal treatment process for drying and crystallizing the spin coated film.

Accordingly, the first object of this invention can be achieved by any of the following non-volatile semiconductor memory cells.

The first one is a non-volatile memory cell comprising :

a field effect transistor further comprising :

a gate comprising a pile of an upper conductive layer and a ferroelectric layer of bismuth titanate containing bismuth more than the stoichiometric quantity, the pile being produced on the surface of a semiconductor layer of one conductivity, and

a set of source and drain of the other conductivity produced in the surface region of the semiconductor layer of one conductivity, at the side of the foregoing gate.

The second one is a non-volatile memory cell comprising :

prising :

a field effect transistor further comprising :

a gate comprising a pile of an upper conductive layer and a ferroelectric layer comprising an upper layer of bismuth titanate of the stoichiometric composition and a lower layer of bismuth titanate containing bismuth more than the stoichiometric quantity, the pile being produced on the surface of a semiconductor layer of one conductivity, and

a set of source and drain of the other conductivity produced in the surface region of the semiconductor layer of one conductivity, at the side of the foregoing gate.

The third one is a non-volatile memory cell comprising :

a field effect transistor further comprising :

a gate comprising a pile of an upper conductive layer, a ferroelectric layer of bismuth titanate containing bismuth more than the stoichiometric quantity, a lower conductive layer and an insulator layer, the pile being produced on the surface of a semiconductor layer of one conductivity, and a set of source and drain of the other conductivity produced in the surface region of the semiconductor layer of one conductivity, at the side of the foregoing gate.

The fourth one is a non-volatile memory cell comprising :

a field effect transistor further comprising :

a gate comprising a pile of an upper conductive layer, a ferroelectric layer comprising an upper layer of bismuth titanate of the stoichiometric composition and a lower layer of bismuth titanate containing bismuth more than the stoichiometric quantity, a lower conductive layer and an insulator layer, the pile being produced on the surface of a semiconductor layer of one conductivity, and

a set of source and drain of the other conductivity produced in the surface region of the semiconductor layer of one conductivity, at the side of the foregoing gate.

The second object of this invention can be achieved by any of the following methods for producing a non-volatile semiconductor memory cell.

The first one is a method for producing a non-volatile semiconductor memory cell comprising :

a step for producing a pile of layers comprising an

upper conductive layer and a ferroelectric layer of bismuth titanate containing bismuth more than the stoichiometric quantity, on the surface of a semiconductor layer of one conductivity, a step for patterning the pile of layers to produce a gate and a step for introducing an impurity of the other conductivity in the semiconductor layer of one conductivity to produce a set of source and drain, at the side of the foregoing gate, to finally produce a field effect transistor, wherein :

the step for producing the ferroelectric layer comprising a step for spin coating an organic solvent solution containing a bismuth source and a titanium source at a mole ratio at which the bismuth component is more than 4 and the titanium component is 3 and a step for applying a thermal treatment process for drying and crystallizing the foregoing spin coated film.

The second one is a method for producing a non-volatile semiconductor memory cell comprising :

a step for producing a pile of layers comprising an upper conductive layer and a ferroelectric layer comprising an upper layer of bismuth titanate of the stoichiometric composition and a lower layer of bismuth titanate containing bismuth more than the stoichiometric quantity, on the surface of a semiconductor layer of one conductivity, a step for patterning the pile of layers to produce a gate and a step for introducing an impurity of the other conductivity in the semiconductor layer of one conductivity to produce a set of source and drain, at the side of the foregoing gate, to finally produce a field effect transistor, wherein :

the step for producing the ferroelectric layer comprising a first step comprising a step for spin coating an organic solvent solution containing a bismuth source and a titanium source at a mole ratio at which the bismuth component is more than 4 and the titanium component is 3 and a step for applying a thermal treatment process for drying and crystallizing the foregoing spin coated film to produce the lower layer and a second step comprising a step for spin coating an organic solvent solution containing a bismuth source and a titanium source at a mole ratio of 4 : 3 and a step for applying a thermal treatment process for drying and crystallizing the foregoing spin coated film to produce the upper layer.

The third one is a method for producing a non-volatile semiconductor memory cell comprising :

a step for producing a pile of layers comprising an upper conductive layer, a ferroelectric layer of bis-

mut titanate containing bismuth more than the stoichiometric quantity, a lower conductive layer and an insulator layer, on the surface of a semiconductor layer of one conductivity, a step for patterning the pile of layers to produce a gate and a step for introducing an impurity of the other conductivity in the semiconductor layer of one conductivity to produce a set of source and drain, at the side of said foregoing gate, to finally produce a field effect transistor, wherein :

the step for producing the ferroelectric layer comprising a step for spin coating an organic solvent solution containing a bismuth source and a titanium source at a mole ratio at which the bismuth component is more than 4 and the titanium component is 3 and a step for applying a thermal treatment process for drying and crystallizing the foregoing spin coated film.

The fourth one is a method for producing a non-volatile semiconductor memory cell comprising :

a step for producing a pile of layers comprising an upper conductive layer, a ferroelectric layer comprising an upper layer of bismuth titanate of the stoichiometric composition and a lower layer of bismuth titanate containing bismuth more than the stoichiometric quantity, a lower conductive layer and an insulator layer, on the surface of a semiconductor layer of one conductivity, a step for patterning the pile of layers to produce a gate and a step for introducing an impurity of the other conductivity in the semiconductor layer of one conductivity to produce a set of source and drain, at the side of the foregoing gate, to finally produce a field effect transistor, wherein :

the step for producing the ferroelectric layer comprising a first step comprising a step for spin coating an organic solvent solution containing a bismuth source and a titanium source at a mole ratio at which the bismuth component is more than 4 and the titanium component is 3 and a step for applying a thermal treatment process for drying and crystallizing the foregoing spin coated film to produce the lower layer and a second step comprising a step for spin coating an organic solvent solution containing a bismuth source and a titanium source at a mole ratio of 4 : 3 and a step for applying a thermal treatment process for drying and crystallizing the foregoing spin coated film to produce the upper layer.

BRIEF DESCRIPTION OF THE DRAWINGS

This invention, together with its various features and advantages, can be readily understood from the fol-

lowing more detailed description presented in conjunction with the following drawings, in which :

Fig. 1 (A) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a first embodiment of this invention, on the way of production,

Fig. 1(B) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a first embodiment of this invention, on the way of production,

Fig. 1 (C) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a first embodiment of this invention, on the way of production,

Fig. 1(D) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a first embodiment of this invention, on the way of production,

Fig. 2(A) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a first embodiment of this invention, on the way of production,

Fig. 2(B) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a first embodiment of this invention, on the way of production,

Fig. 2(C) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a first embodiment of this invention, on the way of production,

Fig. 3(A) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a first embodiment of this invention, on the way of production,

Fig. 3(B) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a first embodiment of this invention, on the way of production,

Fig. 3(C) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a first embodiment of this invention, on the way of production,

Fig. 4(A) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a first embodiment of this invention, on the way of production,

Fig. 4(B) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a first embodiment of this invention, on the way of production,

Fig. 4(C) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a first embodiment of this invention, on the way of production,

Fig. 5(A) is a cross section of a piled layer in which a layer of bismuth titanate of the stoichiometric composition is produced on a layer of bismuth titanate containing bismuth more than the stoichiometric

quantity,

Fig. 5(B) is a cross section of a piled layer in which a layer of bismuth titanate containing bismuth more than the stoichiometric quantity is produced on a layer of bismuth titanate containing bismuth more than the stoichiometric quantity,

Fig. 6(A) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a second embodiment of this invention, on the way of production,

Fig. 6(B) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a second embodiment of this invention, on the way of production,

Fig. 7(A) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a third embodiment of this invention, on the way of production,

Fig. 7(B) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a third embodiment of this invention, on the way of production.

Fig. 8(A) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a fourth embodiment of this invention, on the way of production, and

Fig. 8(B) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a fourth embodiment of this invention, on the way of production.

Fig. 9(A) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a fifth embodiment of this invention, on the way of production,

Fig. 9(B) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a fifth embodiment of this invention, on the way of production,

Fig. 10(A) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a sixth embodiment of this invention, on the way of production,

Fig. 10(B) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a sixth embodiment of this invention, on the way of production,

Fig. 11(A) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a seventh embodiment of this invention, on the way of production,

Fig. 11(B) is a cross section illustrating layer configuration of an MFMIS field effect transistor in accordance with a seventh embodiment of this invention, on the way of production,

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to drawings, a detailed description will be

presented below for non-volatile semiconductor memory cells in accordance with 4 embodiments of this invention.

FIRST EMBODIMENT

A non-volatile semiconductor memory cell employing an MFMIS field effect transistor having a gate of a ruthenium/bismuth titanate of the stoichiometric composition/bismuth titanate containing bismuth more than the stoichiometric quantity /platinum /conductive silicon /silicon dioxide/ silicon structure.

Figs. 1 through 4 illustrate layer configuration of an MFMIS field effect transistor constituting a non-volatile semiconductor memory cell in accordance with a first embodiment of this invention, on the way of production. The drawings are drawn, concentrating an attention to the active region of the MFMIS field effect transistor.

Referring to Fig. 1(A), a LOCOS process or the like is employed to produce a field insulator layer 12 on the surface of a semiconductor (silicon in this embodiment) substrate 10 of one conductivity (p-type in this embodiment), remaining an active area on which an MFMIS field effect transistor is scheduled to be produced, uncovered by the field insulator layer 12. An oxidation process is employed to oxidize the surface region of the p-type silicon substrate 10 to produce a silicon dioxide layer 14 having an approximate thickness of 60 Å, which is scheduled to be a lower insulator layer or a so-called gate insulator layer. A rapid thermal annealer (RTA) is practically employed for the foregoing thermal processes. A reduced pressure chemical vapor deposition process which is conducted by employing monosilane (SiH_4) as the silicon source and phosphine (PH_3) as the source of an n-type impurity, is employed to produce a poly crystalline silicon layer 16 having an approximate thickness of 2000 Å. Thereafter, a thermal treatment process is applied to poly crystalline silicon layer 16 at 850°C to activate the n-type impurity for the purpose to convert the poly crystalline silicon layer 16 to a conductive poly crystalline silicon layer 16 containing an n-type impurity (phosphorus) at the concentration of $4 \times 10^{20} \text{ cm}^{-3}$. A sputtering process is employed to produce a platinum layer 18 having the approximate thickness of 1000 Å. A piled layer of the platinum layer 18 and the conductive poly crystalline silicon layer 16 is scheduled to be employed as a lower conductive layer or a so-called floating gate.

Referring to Fig. 1(B), a first organic solvent solution containing a bismuth source and a titanium source at a mole ratio in which the bismuth component is more than the stoichiometric quantity of bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) or at a mole ratio at which the bismuth component is more than 4 and the titanium component is 3, is spin coated on the surface of the platinum layer 18, and a two-step thermal treatment process is applied to the spin coated film to produce a lower layer of bismuth titanate 20a containing bismuth more than the stoichiometric quantity and having a thickness of e.g. 600 Å.

The direction of the c-axis of the lower layer 20a is perpendicular to the surface of the layer, and the dielectric constant and the remanent polarization are less for the lower layer 20a than for the layer of bismuth titanate of the stoichiometric composition.

The lower layer 20a is scheduled to constitute a ferroelectric layer, when it is combined with an upper layer 20b which will be produced in the later process.

Since the stoichiometric ratio of bismuth and titanium in bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) is 4 : 3, the allowable ratio of bismuth and titanium in the first organic solvent solution is 4.08 through 4.6 : 3, and the appropriate ratio would be 4.4 : 3. The organic solvent solution containing bismuth and titanium at an arbitrary concentration is available at Kabushiki Kaisha Kojundo Kagaku Kenkyusho in Japan under the brand of "a solution employable for producing bismuth titanate by employing a metal organic decomposition method".

When the foregoing spin coating process is conducted, a drop of the first organic solvent solution is dropped on the surface of the platinum layer 18, and the silicon substrate 10 is rotated at 500 rpm for 10 seconds and later at 2500 rpm for 30 seconds.

The foregoing two-step thermal treatment process consists of a first thermal process conducted at 450°C for 15 minutes to dry the spin coated film and a second thermal process conducted in a rapid thermal annealer (RTA) containing dry oxygen at 850°C for 3 minutes to crystallize the dried film for resultantly producing a layer of bismuth titanate containing bismuth more than the stoichiometric quantity and having the thickness of e.g. 600 Å. The crystalline layer of bismuth titanate containing bismuth more than the stoichiometric quantity has the c-axis perpendicular to the surface of the layer and has the dielectric constant and the remanent polarization smaller than those of bismuth titanate of the stoichiometric composition.

The foregoing second thermal process conducted in a RTA can be replaced by a thermal treatment process conducted in the dry oxygen of 850°C for 30 minutes in an ordinary electric furnace.

Referring to Fig. 1(C), a second organic solvent solution containing a bismuth source and a titanium source in the stoichiometric ratio of bismuth titanate or in the ratio of 4 : 3 is spin coated on the lower layer 20a, and a two-step thermal treatment process is applied to the spin coated film to produce the first layer 20b1 of an upper layer 20b of bismuth titanate of the stoichiometric composition and having a thickness of e.g. 600 Å.

When the foregoing spin coating process is conducted, a drop of the second organic solvent solution is dropped on the surface of the lower layer 20a of bismuth titanate containing bismuth more than the stoichiometric quantity, and silicon substrate 10 is rotated at 500 rpm for 10 seconds and later at 2500 rpm for 30 seconds.

The foregoing two-step thermal treatment process consists of a first thermal process conducted at 450 °C for 15 seconds to dry the spin coated film and a second thermal process conducted in a rapid thermal annealer

(RTA) of 850°C for 3 minutes to crystallize the dried film for producing a bismuth titanate of the stoichiometric composition or the first layer 20b1 of bismuth titanate of the stoichiometric composition. The direction of the c-axis of the lower layer 20a which is perpendicular to the surface of the layer is taken over by the first layer 20b1 of bismuth titanate of the stoichiometric composition. As a result, the c-axis of the first layer 20b1 of bismuth titanate of the stoichiometric composition directs perpendicular to the surface of the layer, and the dielectric constant and the remanent polarization of the first layer 20b1 of bismuth titanate of the stoichiometric composition is less than those of bismuth titanate of the stoichiometric composition.

Referring to Fig. 1(D), the foregoing process for producing a layer of bismuth titanate of the stoichiometric composition is repeated to produce the second and later layers 20b2 through 20b4 of bismuth titanate of the stoichiometric composition. Since the direction of the c-axis of the first layer 20b1 is taken over by the second and later layers 20b2 through 20b4 of bismuth titanate of the stoichiometric composition, these layers 20b2 through 20b4 have dielectric constant and remanent polarization less than those of bismuth titanate of the stoichiometric composition.

Referring to Fig. 2(A), a pile of the lower layer of bismuth titanate 20a containing bismuth more than the stoichiometric quantity and having dielectric constant and remanent polarization less than bismuth titanate of the stoichiometric composition and the upper layer of bismuth titanate 20b consisting of the second through fourth layers 20b1 through 20b4 of bismuth titanate of the stoichiometric composition which has dielectric constant and remanent polarization less than the ordinary bismuth titanate crystal, constitutes a ferroelectric layer 20 which has the thickness of e.g. 3000 Å and which has dielectric constant and remanent polarization less than the ordinary bismuth titanate crystal.

Referring to Fig. 2(B), a sputtering process is employed to produce a layer of ruthenium 22 having the thickness of 2000 Å on the ferroelectric layer 20. The ruthenium layer 22 is scheduled to be an upper conductive layer or a so-called gate electrode.

Referring to Fig. 2(C), a chemical vapor deposition process is employed to produce a layer of silicon dioxide 24 on the ruthenium layer 22. The silicon dioxide layer 24 is scheduled to be an etching mask for producing a gate out of a pile of the ruthenium layer 22, the ferroelectric layer 20, the platinum layer 18, the conductive silicon layer 16 and the silicon dioxide layer 14.

Referring to Fig. 3(A), a photolithography process is employed to pattern the silicon dioxide layer 24 into the horizontal shape of a gate electrode to produce an etching mask 24X. A dry etching process employing CCl_4 or CF_4 as the etchant gas is applied to the ruthenium layer 22 and the ferroelectric layer 20 by employing the etching mask 24X to pattern these layers 22 and 20 into the horizontal shape of the gate electrode. A reactive ion etching process employing a magnetron reactive etch-

ing equipment is practically employed for this process to improve the throughput or the etching rate.

Referring to Fig. 3(B), an ion milling process is employed to pattern the platinum layer 18 into the horizontal shape of a gate electrode. The patterned layer of platinum 18X is scheduled to act as the upper layer of a lower conductive layer, together with a patterned layer 16X of poly crystalline conductive silicon. By this ion milling process, the thickness of the etching mask 24X is remarkably decreased.

Referring to Fig. 3(C), a dry etching process employing CCl_4 or CF_4 as the etchant is employed to pattern the conductive poly crystalline silicon layer 16 and the silicon dioxide layer 14 into the horizontal shape of the gate electrode. The patterned layer 16X of the conductive poly crystalline silicon layer 16 is scheduled to act as the lower layer of the lower conductive layer, together with patterned platinum layer 18X. The patterned silicon dioxide layer 14X is scheduled to act as the so-called gate insulator layer. By this dry etching process, the etching mask 24X is entirely removed.

By the foregoing processes, a gate consisting of a ruthenium layer 22X acting as the upper conductive layer, a ferroelectric layer 20X consisting of an upper layer 20bX of a piled layer of bismuth titanate of the stoichiometric composition and a lower layer 20aX of bismuth titanate containing bismuth more than the stoichiometric quantity, a lower conductive layer consisting of a platinum layer 18X and a conductive poly crystalline silicon layer 16X and a silicon dioxide layer 14X, has been produced.

Referring to Fig. 4(A), a low temperature chemical vapor deposition process is employed to cover the entire surface of a field effect transistor under production with a silicon dioxide layer 26. An anisotropic etching process is employed to expose the area on which a source and a drain are scheduled to be produced. A reactive ion etching process can be employed as the anisotropic etching method employable for this process.

Referring to Fig. 4(B), an ion implantation process is employed to introduce an n-type impurity e.g. phosphorus, arsenic or antimony to produce a source 28a and a drain 28b. The reason why this ion implantation process is conducted after the processes for producing the silicon dioxide layer 26 and for patterning the same is to cover the side surface of the ferroelectric layer 20X for the ultimate purpose to protect the side surface of the ferroelectric layer 20X from potential damages caused by the implantation process. Since the thickness of the silicon dioxide layer 26 deposited on the side surface of the patterned piled layers does not exceed 2000 Å, and since the source 28a and the drain 28b laterally diffuse toward under the patterned piled layers, there is no possibilities in which the source 28a and the drain 28b fail to contact a channel which occurs under a gate.

Referring to Fig. 4(C), a chemical vapor deposition process is employed to cover the entire surface of the field effect transistor under production with a silicon dioxide layer or a phosphor-silicate glass layer 32. After

contact holes 30 are produced to reach the source 28a and the drain 28b, a selected tungsten chemical vapor deposition process is employed to produce a tungsten layer 34 on the entire surface of the field effect transistor under production. Thereafter, the tungsten layer 34 is removed, remaining it in the contact holes 30 to berry it. Finally, an aluminum layer is deposited and patterned to produce aluminum wires 36 which connect the source 28a and the drain 28b with external circuits.

The foregoing process has successfully produced a non-volatile semiconductor memory cell employing an MFMS field effect transistor having a gate made of an upper conductive layer of ruthenium, a ferroelectric layer consisting of an upper layer of bismuth titanate of the stoichiometric composition but which has dielectric constant and remanent polarization less than those of bismuth titanate of the stoichiometric composition and a lower layer of bismuth titanate containing bismuth more than the stoichiometric quantity and which has dielectric constant and remanent polarization less than those of bismuth titanate of the stoichiometric composition, a lower conductive layer consisting of an upper layer of platinum and a lower layer of conductive poly crystalline silicon and an insulator layer of silicon dioxide, produced on the surface of a silicon layer or substrate of one conductivity, and a set of source and drain of the other conductivity produced in the surface region of the silicon layer, or substrate of one conductivity, at the side of the gate, the non-volatile semiconductor memory cell being a non-volatile semiconductor memory cell in accordance with the first embodiment of this invention.

Since the foregoing ferroelectric layer consisting of an upper layer of bismuth titanate of the stoichiometric composition and a lower layer of bismuth titanate containing bismuth more than the stoichiometric quantity has a c-axis perpendicular to the surface of the layer and has a less amount of dielectric constant and remanent polarization, the foregoing field effect transistor is allowed to generate a large magnitude of the intensity of electric field, when it is applied even a less amount of voltage applied to the upper conductive layer of the gate. As a result, a non-volatile memory cell in accordance with the first embodiment of this invention is allowed to memorize or erase binary information with a less amount of the writing or erasing voltage which is to be applied between the gate electrode and the semiconductor substrate.

The electromagnetic characteristics of bismuth titanate containing bismuth more than the stoichiometric quantity has been experimentally determined.

Test pieces were produced by producing a ruthenium layer of 2000 Å thick on a layer of bismuth titanate which contains bismuth more than the stoichiometric quantity and which was produced by employing an organic solvent solution containing a bismuth source and a titanium source at a ratio of 4.4 : 3, the layer of bismuth titanate being produced on a platinum layer of 600 Å thick, the platinum layer being produced on a silicon dioxide layer of 2000 Å thick, the silicon dioxide

layer being produced on a p-type silicon substrate. Hysteresis characteristics were measured by employing Sawyer-tower circuit for the layer of bismuth titanate containing bismuth more than the stoichiometric quantity. The ruthenium layer and the platinum layer were employed as the electrodes. Paying an attention to the difference in work function between platinum and ruthenium, the amount of remanent polarization was determined to be approximately $1.8 \mu\text{C}/\text{cm}^2$. The amount of dielectric constant and coercive field were determined to be approximately 67 and 12 KV/cm. Since bismuth titanate of the stoichiometric composition has the dielectric constant of 180, the remanent polarization of $4.4 \mu\text{C}/\text{cm}^2$ and the coercive field of 84 KV/cm, and also since lead zirconate titanate has the dielectric constant of 875, the remanent polarization of $25.4 \mu\text{C}/\text{cm}^2$ and the coercive field of 57.5 KV/cm, bismuth titanate containing bismuth more than the stoichiometric quantity was determined to be more appropriate as the ferroelectric material to be used for a field effect transistor in accordance with this invention than any of the ferroelectric materials available in the prior art. Accordingly, the field effect transistor in accordance with this invention is allowed to generate a sufficiently large amount of intensity of electric field by being applied a less voltage between the gate electrode and the semiconductor substrate.

Further, since bismuth titanate has a small amount of coercive field, the hysteresis characteristics are readily saturated by a less amount of the voltage to be applied to the gate, resultantly causing a less possibility of breakdown for the insulator layer arranged between the lower conductive layer and the semiconductor substrate.

Flatness was observed for the surface of a layer of bismuth titanate containing bismuth more than the stoichiometric quantity. For this purpose, two test pieces were produced. The first one has a layer 3 of bismuth titanate of the stoichiometric composition produced on the surface of a layer 2 of bismuth titanate containing bismuth more than the stoichiometric quantity, the latter layer 2 of bismuth titanate being produced on a layer 1 of platinum. The second one has a layer 2 of bismuth titanate containing bismuth more than the stoichiometric quantity produced on the surface of the latter layer 2 of bismuth titanate containing bismuth more than the stoichiometric quantity, the latter layer 2 of bismuth titanate being produced on a layer 1 of platinum. The cross section of the two test pieces was observed with magnification of 20,000 by employing a scanning electronic microscope (SEM).

The result of the observation for the first one is illustrated in Fig. 5(A), and the result of the observation for the second one is illustrated in Fig. 5(B). Fig. 5(A) clearly shows a surface more flat than the surface shown in Fig. 5(B). As a result, it is clear that no local concentration of electric field occurs for the layer of bismuth titanate of the stoichiometric quantity produced on the layer of bismuth titanate containing bismuth more

than the stoichiometric quantity.

SECOND EMBODIMENT

A non-volatile semiconductor memory cell of an MFMS field effect transistor having a gate of a ruthenium/bismuth titanate of the stoichiometric composition/bismuth titanate containing bismuth more than the stoichiometric quantity/ruthenium dioxide/ruthenium/conductive silicon/silicon dioxide/ silicon structure.

Figs. 6(A) and (B) illustrate layer configuration of an MFMS field effect transistor constituting a non-volatile semiconductor memory cell in accordance with a second embodiment of this invention, on the way of production.

Referring to Fig. 6(A), the steps to be employed for producing a field insulator layer 12, a silicon dioxide layer 14 and a conductive poly crystalline silicon layer 16, in this order, on a p-type silicon substrate 10 are identical to the corresponding steps employed in the process for the first embodiment of this invention. A sputtering process is employed to produce a layer of ruthenium 18a having an approximate thickness of 500 Å on the conductive poly crystalline silicon layer 16. Thereafter, a sputtering process is employed to produce a layer of ruthenium dioxide 18b having an approximate thickness of 1000 Å on the ruthenium layer 18a. A piled layer 18 of the ruthenium dioxide layer 18b and the ruthenium layer 18a, in combination with the conductive poly crystalline silicon layer 16, is allowed to act as a lower conductive layer or a so-called floating gate. A ferroelectric layer 20 consisting of a layer 20a of bismuth titanate containing bismuth more than the stoichiometric quantity and having a less amount of dielectric constant and remanent polarization and a layer 20b of bismuth titanate of the stoichiometric composition but having a less amount of dielectric constant and remanent polarization is produced by employing the corresponding steps employed in the process for the first embodiment of this invention.

The function of the ruthenium dioxide layer 18b is to compensate oxygen vacancy which often occurs in a ferroelectric material on the occasion that a ferroelectric layer had been fatigued. In other words, since the ferroelectric layer 20 is contacted by an oxide layer, specifically the ruthenium dioxide layer 18b, oxygen vacancy can readily be compensated. On the other hand, the function of the ruthenium layer 18a is to prevent the conductive poly crystalline silicon layer 16 from being oxidized and to improve the adhesion between the ruthenium dioxide layer 18b and the conductive poly crystalline silicon layer 16.

A sputtering process is employed to produce a layer of ruthenium 22 on the ferroelectric layer 20.

Referring to Fig. 6(B), a dry etching process employing CCl_4 or CF_4 as the etchant is employed to pattern a piled layer consisting of the ruthenium layer 22, the ferroelectric layer 20, the piled layer 18 of the ruthenium dioxide layer 18b and the ruthenium layer

18a, the conductive poly crystalline silicon layer 16 and the silicon dioxide layer 14, into the horizontal shape of the gate electrode. Since ruthenium and ruthenium dioxide can be readily etched by employing a dry etching process, the foregoing piled layer can be patterned with a single step. It is needless to emphasize that the process is remarkably simplified. Incidentally, since a dry etching process allows more minute etching accuracy than an ion milling process, a larger magnitude of integration can be expected for the non-volatile semiconductor memory cell employing the MFMS field effect transistor in accordance with the second embodiment of this invention. The suffix "x" added to each layer indicates the patterned layer.

THIRD EMBODIMENT

A non-volatile semiconductor memory cell of an MFMS field effect transistor having a gate of a ruthenium/bismuth titanate of the stoichiometric composition/bismuth titanate containing bismuth more than the stoichiometric quantity/bismuth titanate of the stoichiometric composition/ ruthenium dioxide/ruthenium/conductive silicon/silicon dioxide/silicon structure.

Figs. 7(A) and (B) illustrate layer configuration of an MFMS field effect transistor constituting a non-volatile semiconductor memory cell in accordance with a third embodiment of this invention, on the way of production.

Referring to Fig. 7(A), the steps to be employed for producing a field insulator layer 12, a silicon dioxide layer 14, a conductive poly crystalline silicon layer 16, a ruthenium layer 18a and a ruthenium dioxide layer 18b, in this order, on a p-type silicon substrate 10 are identical to the corresponding steps employed in the process for the second embodiment of this invention. A layer of bismuth titanate of the stoichiometric composition 19 is produced on the ruthenium dioxide layer 18b by employing a process identical to the process employed for producing the layer of bismuth titanate of the stoichiometric composition 20b1 in the first embodiment of this invention. The function of the layer of bismuth titanate of the stoichiometric composition 19 is to improve the flatness of the surface of the ruthenium dioxide layer 18b which is inclined to be slightly rough. Although the layer of bismuth titanate of the stoichiometric composition 19 does not have a less amount of dielectric constant and remanent polarization, it is effective to improve the flatness of the surface of the ruthenium dioxide layer 18b. A ferroelectric layer 20 and a ruthenium layer 22 are produced on the layer of bismuth titanate of the stoichiometric composition 19 by employing a process identical to the process employed for producing the ferroelectric layer 20 and a ruthenium layer 22 in the first and second embodiments of this invention.

Referring to Fig. 7(B), a dry etching process employing CCl_4 or CF_4 as the etchant is employed to pattern a piled layer consisting of the ruthenium layer 22, the ferroelectric layer 20, the layer of bismuth titanate of the stoichiometric composition 19, the piled layer

18 of the ruthenium dioxide layer 18b and the ruthenium layer 18a, the conductive poly crystalline silicon layer 16 and the silicon dioxide layer 14, into the horizontal shape of the gate electrode. The suffix "x" added to each layer indicates the patterned layer.

FOURTH EMBODIMENT

A non-volatile semiconductor memory cell of an MFMIS field effect transistor having a gate of a ruthenium/bismuth titanate of the stoichiometric composition/bismuth titanate containing bismuth more than the stoichiometric quantity/bismuth titanate containing titanium more than the stoichiometric quantity / ruthenium dioxide /ruthenium /conductive silicon /silicon dioxide /silicon structure.

Figs. 8(A) and (B) illustrate layer configuration of an MFMIS field effect transistor constituting a non-volatile semiconductor memory cell in accordance with a fourth embodiment of this invention, on the way of production.

Referring to Fig. 8(A), the steps to be employed for producing a field insulator layer 12, a silicon dioxide layer 14, a conductive poly crystalline silicon layer 16, a ruthenium layer 18a and a ruthenium dioxide layer 18b, in this order, on a p-type silicon substrate 10 are identical to the corresponding steps employed in the process for the second embodiment of this invention. A layer of bismuth titanate containing titanium more than the stoichiometric quantity 23 is produced on the ruthenium dioxide layer 18b by employing a process which is similar to the process employed for producing the layer of bismuth titanate containing bismuth more than the stoichiometric quantity employed in the first embodiment of this invention but which employs an organic solvent solution containing titanium more than the stoichiometric quantity.

The layer configuration of and the process for producing an MFMIS field effect transistor constituting a non-volatile semiconductor memory cell in accordance with the fourth embodiment of this invention are entirely identical to those for the third embodiment of this invention, excepting that the layer of bismuth titanate of the stoichiometric composition 19 is replaced by a layer of bismuth titanate containing titanium more than the stoichiometric quantity 23 and that the organic solvent solution containing a bismuth source and a titanium source at a mole ratio of 4 : 3 is replaced by an organic solvent solution containing a bismuth source and a titanium source at a mole ratio at which the titanium component is more than 3 and the bismuth component is 4. The results specific to this embodiment are that the ferroelectric layer is more flat in this embodiment than in the third embodiment and that a leak current flowing in the ferroelectric layer is less in this embodiment than in the third embodiment.

FIFTH EMBODIMENT

A non-volatile semiconductor memory cell of an MFMIS

field effect transistor having a gate of an iridium dioxide / bismuth titanate of the stoichiometric composition/bismuth titanate containing bismuth more than the stoichiometric quantity / iridium dioxide / iridium / conductive silicon / silicon dioxide / silicon structure.

Figs. 9(A) and (B) illustrate layer configuration of an MFMIS field effect transistor constituting a non-volatile semiconductor memory cell in accordance with a fifth embodiment of this invention, on the way of production.

Referring to Fig. 9(A), the steps to be employed for producing a field insulator layer 12, a silicon dioxide layer 14 and a conductive poly crystalline silicon layer 16, in this order, on a p-type silicon substrate 10 are identical to the corresponding steps employed in the process for the first embodiment of this invention. A sputtering process is employed to produce a layer of iridium 26a having an approximate thickness of 500 Å on the conductive poly crystalline silicon layer 16. Thereafter, a sputtering process is employed to produce a layer of iridium dioxide 26b having an approximate thickness of 1000 Å on the iridium layer 26a. A piled layer 26 of the iridium dioxide layer 26b and the iridium layer 26a, in combination with the conductive poly crystalline silicon layer 16, is allowed to act as a lower conductive layer or a so-called floating gate. A ferroelectric layer 20 consisting of a layer 20a of bismuth titanate containing bismuth more than the stoichiometric quantity and having a less amount of dielectric constant and remanent polarization and a layer 20b of bismuth titanate of the stoichiometric composition but having a less amount of dielectric constant and remanent polarization is produced by employing the corresponding steps employed in the process for the first embodiment of this invention.

The function of the iridium dioxide layer 26b is to compensate oxygen vacancy which often occurs in a ferroelectric material on the occasion that a ferroelectric layer had been fatigued. In other words, since the ferroelectric layer 20 is contacted by an oxide layer, specifically the iridium dioxide layer 26b, oxygen vacancy can readily be compensated. On the other hand, the function of the iridium layer 26a is to prevent the conductive poly crystalline silicon layer 16 from being oxidized and to improve the adhesion between the iridium dioxide layer 26b and the conductive poly crystalline silicon layer 16.

A sputtering process is employed to produce a layer of iridium oxide 28 on the ferroelectric layer 20.

Referring to Fig. 9(B), a dry etching process employing CCl_4 or CF_4 as the etchant is employed to pattern a piled layer consisting of the iridium oxide layer 28, the ferroelectric layer 20, the piled layer 26 of the iridium dioxide layer 26b and the iridium layer 26a, the conductive poly crystalline silicon layer 16 and the silicon dioxide layer 14, into the horizontal shape of the gate electrode. Since iridium and iridium dioxide can be readily etched by employing a dry etching process, the foregoing piled layer can be patterned with a single step. It is needless to emphasize that the process is

remarkably simplified. Incidentally, since a dry etching process allows more minute etching accuracy than an ion milling process, a larger magnitude of integration can be expected for the non-volatile semiconductor memory cell employing the MFMS field effect transistor in accordance with the fifth embodiment of this invention. The suffix "x" added to each layer indicates the patterned layer.

SIXTH EMBODIMENT

A non-volatile semiconductor memory cell of an MFMS field effect transistor having a gate of an iridium dioxide /bismuth titanate of the stoichiometric composition/bismuth titanate containing bismuth more than the stoichiometric quantity/bismuth titanate of the stoichiometric composition / iridium dioxide / iridium / conductive silicon/ silicon dioxide / silicon structure.

Figs. 10(A) and (B) illustrate layer configuration of an MFMS field effect transistor constituting a non-volatile semiconductor memory cell in accordance with a sixth embodiment of this invention, on the way of production.

Referring to Fig. 10(A), the steps to be employed for producing a field insulator layer 12, a silicon dioxide layer 14, a conductive poly crystalline silicon layer 16, an iridium layer 26a and an iridium dioxide layer 26b, in this order, on a p-type silicon substrate 10 are identical to the corresponding steps employed in the process for the second embodiment of this invention. A layer of bismuth titanate of the stoichiometric composition 19 is produced on the iridium dioxide layer 26b by employing a process identical to the process employed for producing the layer of bismuth titanate of the stoichiometric composition 20b1 in the first embodiment of this invention. The function of the layer of bismuth titanate of the stoichiometric composition 19 is to improve the flatness of the surface of the iridium dioxide layer 26b which is inclined to be slightly rough. Although the layer of bismuth titanate of the stoichiometric composition 19 does not have a less amount of dielectric constant and remanent polarization, it is effective to improve the flatness of the surface of the iridium dioxide layer 26b. A ferroelectric layer 20 and an iridium dioxide layer 28 are produced on the layer of bismuth titanate of the stoichiometric composition 19 by employing a process identical to the process employed for producing the ferroelectric layer 20 and a ruthenium layer 22 in the first and second embodiments of this invention.

Referring to Fig. 10(B), a dry etching process employing CCl_4 or CF_4 as the etchant is employed to pattern a piled layer consisting of the iridium dioxide layer 28, the ferroelectric layer 20, the layer of bismuth titanate of the stoichiometric composition 19, the piled layer 26 of the iridium dioxide layer 26b and the iridium layer 26a, the conductive poly crystalline silicon layer 16 and the silicon dioxide layer 14, into the horizontal shape of the gate electrode. The suffix "x" added to each layer indicates the patterned layer.

SEVENTH EMBODIMENT

A non-volatile semiconductor memory cell of an MFMS field effect transistor having a gate of an iridium dioxide /bismuth titanate of the stoichiometric composition/bismuth titanate containing bismuth more than the stoichiometric quantity/bismuth titanate containing titanium more than the stoichiometric quantity / iridium dioxide / iridium / conductive silicon /silicon dioxide /silicon structure.

Figs. 11(A) and (B) illustrate layer configuration of an MFMS field effect transistor constituting a non-volatile semiconductor memory cell in accordance with a seventh embodiment of this invention, on the way of production.

Referring to Fig. 11(A), the steps to be employed for producing a field insulator layer 12, a silicon dioxide layer 14, a conductive poly crystalline silicon layer 16, an iridium layer 26a and an iridium dioxide layer 26b, in this order, on a p-type silicon substrate 10 are identical to the corresponding steps employed in the process for the second embodiment of this invention. A layer of bismuth titanate containing titanium more than the stoichiometric quantity 23 is produced on the iridium dioxide layer 26b by employing a process which is similar to the process employed for producing the layer of bismuth titanate containing bismuth more than the stoichiometric quantity employed in the first embodiment of this invention but which employs an organic solvent solution containing titanium more than the stoichiometric quantity.

The layer configuration of and the process for producing an MFMS field effect transistor constituting a non-volatile semiconductor memory cell in accordance with the seventh embodiment of this invention are entirely identical to those for the third embodiment of this invention, excepting that the layer of bismuth titanate of the stoichiometric composition 19 is replaced by a layer of bismuth titanate containing titanium more than the stoichiometric quantity 23 and that the organic solvent solution containing a bismuth source and a titanium source at a mole ratio of 4 : 3 is replaced by an organic solvent solution containing a bismuth source and a titanium source at a mole ratio at which the titanium component is more than 3 and the bismuth component is 4. The results specific to this embodiment are that the ferroelectric layer is more flat in this embodiment than in the sixth embodiment and that a leak current flowing in the ferroelectric layer is less in this embodiment than in the sixth embodiment.

The foregoing description has clarified that a non-volatile semiconductor memory cell employing an MFS or MFMS field effect transistor which allows a less amount of voltage to be applied between the gate electrode and the semiconductor substrate, to write a piece of binary information therein and to erase the piece of binary information therefrom and a method for producing it, are successfully provided by this invention.

Although this invention has been described with reference to specific embodiments, this description is not

meant to be construed in a limiting sense. Various modifications of the disclosed embodiments, as well as other embodiments of this invention, will be apparent to persons skilled in the art upon reference to the description of this invention. It is therefore contemplated that the appended claims will cover any such modifications or embodiments as fall within the true scope of this invention.

Claims

1. A non-volatile semiconductor memory cell comprising :

a field effect transistor further comprising :

a gate comprising a pile of an upper conductive layer and a ferroelectric layer of bismuth titanate containing bismuth more than the stoichiometric quantity, said pile being produced on the surface of a semiconductor layer of one conductivity, and a set of source and drain of the other conductivity produced in the surface region of said semiconductor layer of one conductivity, at the side of said gate.

2. A non-volatile semiconductor memory cell comprising :

a field effect transistor further comprising :

a gate comprising a pile of an upper conductive layer and a ferroelectric layer comprising an upper layer of bismuth titanate of the stoichiometric composition and a lower layer of bismuth titanate containing bismuth more than the stoichiometric quantity, said pile being produced on the surface of a semiconductor layer of one conductivity, and a set of source and drain of the other conductivity produced in the surface region of said semiconductor layer of one conductivity, at the side of said gate.

3. A non-volatile semiconductor memory cell comprising :

a field effect transistor further comprising :

a gate comprising a pile of an upper conductive layer, a ferroelectric layer of bismuth titanate containing bismuth more than the stoichiometric quantity, a lower conductive layer and an insulator layer, said pile being produced on the surface of a semiconductor layer of one conductivity, and a set of source and drain of the other

conductivity produced in the surface region of said semiconductor layer of one conductivity, at the side of said gate.

4. A non-volatile semiconductor memory cell comprising :

a field effect transistor further comprising :

a gate comprising a pile of an upper conductive layer, a ferroelectric layer comprising an upper layer of bismuth titanate of the stoichiometric composition and a lower layer of bismuth titanate containing bismuth more than the stoichiometric quantity, a lower conductive layer and an insulator layer, said pile being produced on the surface of a semiconductor layer of one conductivity, and

a set of source and drain of the other conductivity produced in the surface region of said semiconductor layer of one conductivity, at the side of said gate.

5. A non-volatile semiconductor memory cell in accordance with claim 3 or 4, wherein said lower conductive layer comprising a platinum layer.

6. A non-volatile semiconductor memory cell in accordance with claim 3 or 4, wherein said lower conductive layer comprising a piled layer of a ruthenium dioxide layer and a ruthenium layer.

7. A non-volatile semiconductor memory cell in accordance with claim 6, wherein a layer of bismuth titanate of the stoichiometric composition is arranged between said ferroelectric layer and said lower conductive layer.

8. A non-volatile semiconductor memory cell in accordance with claim 6, wherein a layer of bismuth titanate containing titanium more than the stoichiometric quantity is arranged between said ferroelectric layer and said lower conductive layer.

9. A non-volatile semiconductor memory cell in accordance with claim 3 or 4, wherein said lower conductive layer comprising a piled layer of an iridium dioxide layer and an iridium layer.

10. A non-volatile semiconductor memory cell in accordance with claim 9, wherein a layer of bismuth titanate of the stoichiometric composition is arranged between said ferroelectric layer and said lower conductive layer.

11. A non-volatile semiconductor memory cell in accordance with claim 9, wherein a layer of bismuth titanate containing titanium more than the stoichiometric

metric quantity is arranged between said ferroelectric layer and said lower conductive layer.

12. A method for producing a non-volatile semiconductor memory cell comprising :

a step for producing a pile of layers comprising an upper conductive layer and a ferroelectric layer of bismuth titanate containing bismuth more than the stoichiometric quantity, on the surface of a semiconductor layer of one conductivity, a step for patterning said pile of layers to produce a gate, and a step for introducing an impurity of the other conductivity in said semiconductor layer of one conductivity to produce a set of source and drain, at the side of said gate, to finally produce a field effect transistor, wherein :

the step for producing said ferroelectric layer comprising a step for spin coating an organic solvent solution containing a bismuth source and a titanium source at a mole ratio at which the bismuth component is more than 4 and the titanium component is 3 and a step for applying a thermal treatment process for drying and crystallizing the spin coated film.

13. A method for producing a non-volatile semiconductor memory cell comprising :

a step for producing a pile of layers comprising an upper conductive layer and a ferroelectric layer comprising an upper layer of bismuth titanate of the stoichiometric composition and a lower layer of bismuth titanate containing bismuth more than the stoichiometric quantity, on the surface of a semiconductor layer of one conductivity, a step for patterning said pile of layers to produce a gate and a step for introducing an impurity of the other conductivity in said semiconductor layer of one conductivity to produce a set of source and drain, at the side of said gate, to finally produce a field effect transistor, wherein :

the step for producing said ferroelectric layer comprising a first step comprising a step for spin coating an organic solvent solution containing a bismuth source and a titanium source at a mole ratio at which the bismuth component is more than 4 and the titanium component is 3 and a step for applying a thermal treatment process for drying and crystallizing the spin coated film to produce said lower layer and a second step comprising a step for spin coating an organic solvent solution containing a bis-

muth source and a titanium source at a mole ratio of 4 : 3 and a step for applying a thermal treatment process for drying and crystallizing the spin coated film to produce said upper layer.

14. A method for producing a non-volatile semiconductor memory cell comprising :

a step for producing a pile of layers comprising an upper conductive layer, a ferroelectric layer of bismuth titanate containing bismuth more than the stoichiometric quantity, a lower conductive layer and an insulator layer, on the surface of a semiconductor layer of one conductivity, a step for patterning said pile of layers to produce a gate and a step for introducing an impurity of the other conductivity in said semiconductor layer of one conductivity to produce a set of source and drain, at the side of said gate, to finally produce a field effect transistor, wherein :

the step for producing said ferroelectric layer comprising a step for spin coating an organic solvent solution containing a bismuth source and a titanium source at a mole ratio at which the bismuth component is more than 4 and the titanium component is 3 and a step for applying a thermal treatment process for drying and crystallizing the spin coated film.

15. A method for producing a non-volatile semiconductor memory cell comprising :

a step for producing a pile of layers comprising an upper conductive layer, a ferroelectric layer comprising an upper layer of bismuth titanate of the stoichiometric composition and a lower layer of bismuth titanate containing bismuth more than the stoichiometric quantity, a lower conductive layer and an insulator layer, on the surface of a semiconductor layer of one conductivity, a step for patterning said pile of layers to produce a gate and a step for introducing an impurity of the other conductivity in said semiconductor layer of one conductivity to produce a set of source and drain, at the side of said gate, to finally produce a field effect transistor, wherein :

the step for producing said ferroelectric layer comprising a first step comprising a step for spin coating an organic solvent solution containing a bismuth source and a titanium source at a mole ratio at which the bismuth component is more than 4 and the titanium component is 3 and a step for

applying a thermal treatment process for
drying and crystallizing the spin coated film
to produce said lower layer and a second
step comprising a step for spin coating an
organic solvent solution containing a bis- 5
muth source and a titanium source at a
mole ratio of 4 : 3 and a step for applying a
thermal treatment process for drying and
crystallizing the spin coated film to pro-
duce said upper layer. 10

15

20

25

30

35

40

45

50

55

FIG. 1 (A)

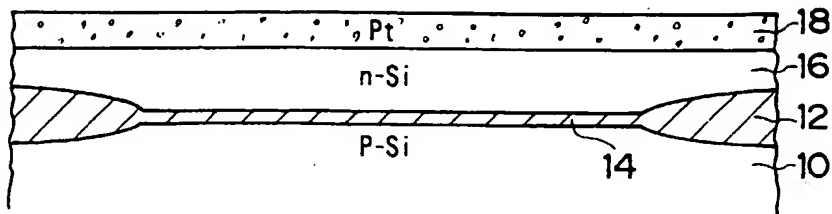


FIG. 1 (B)

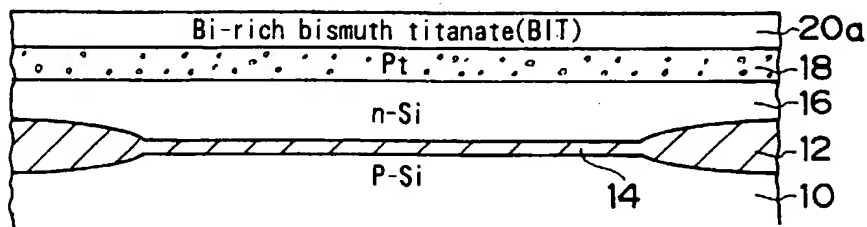


FIG. 1 (C)

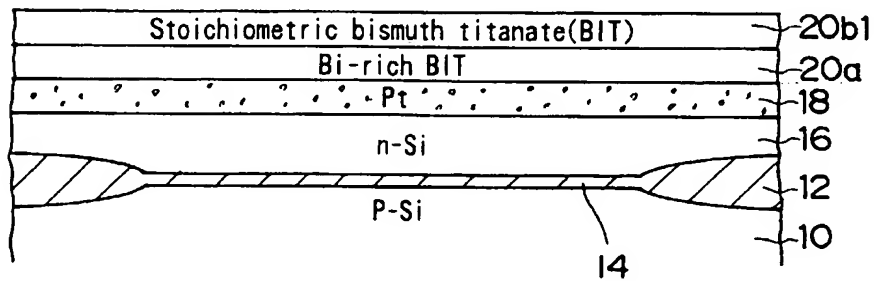


FIG. 1 (D)

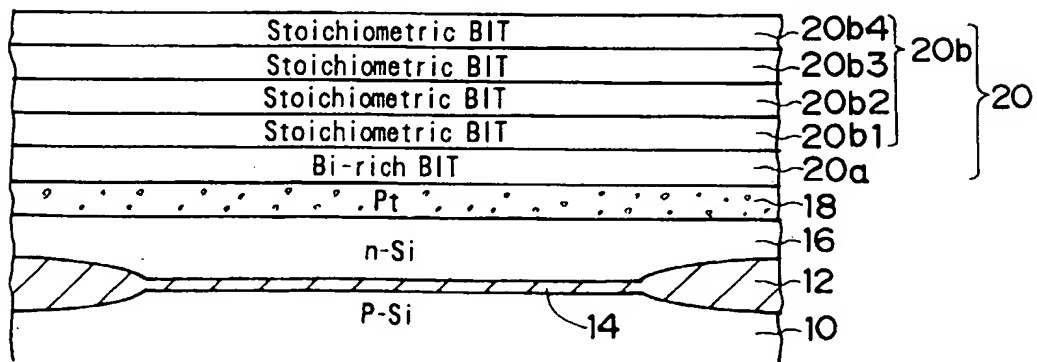


FIG. 2 (A)

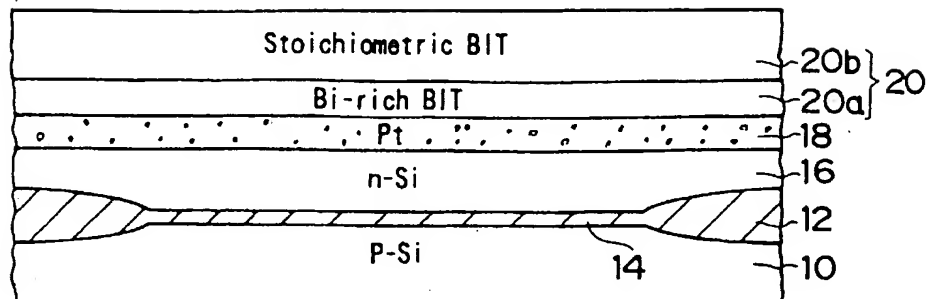


FIG. 2 (B)

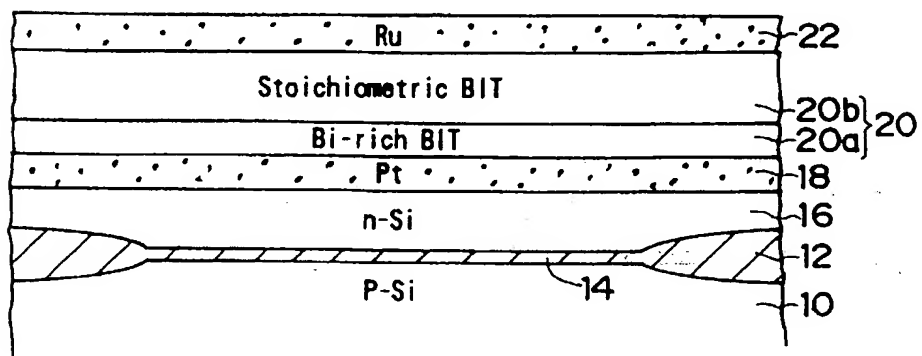


FIG. 2 (C)

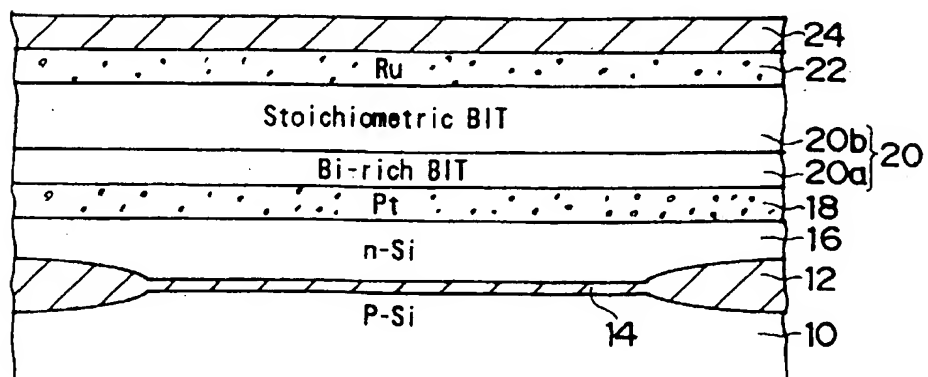


FIG. 3 (A)

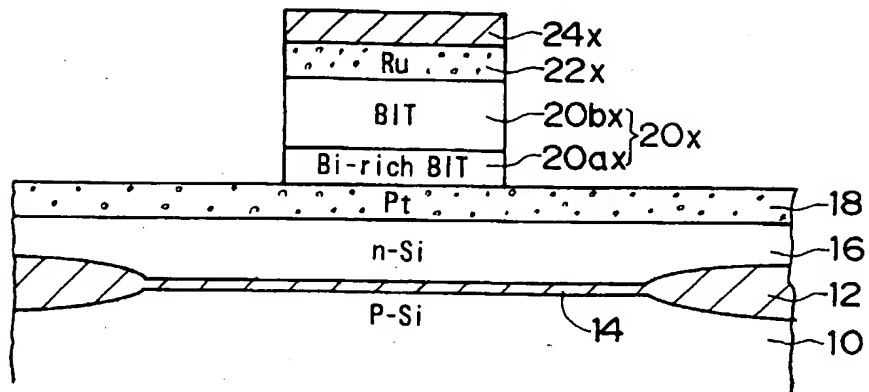


FIG. 3 (B)

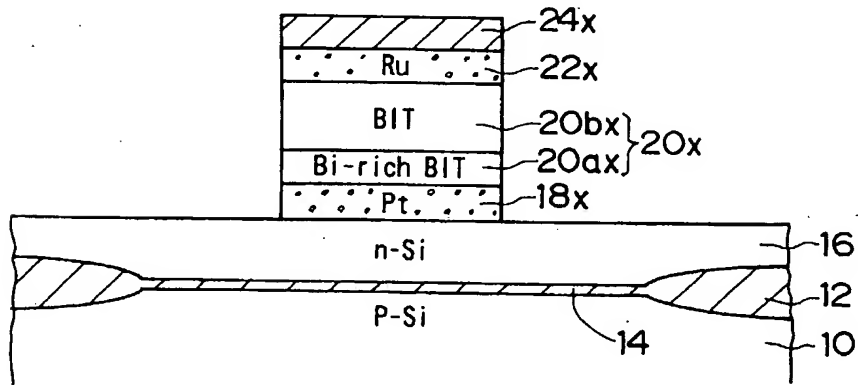


FIG. 3 (C)

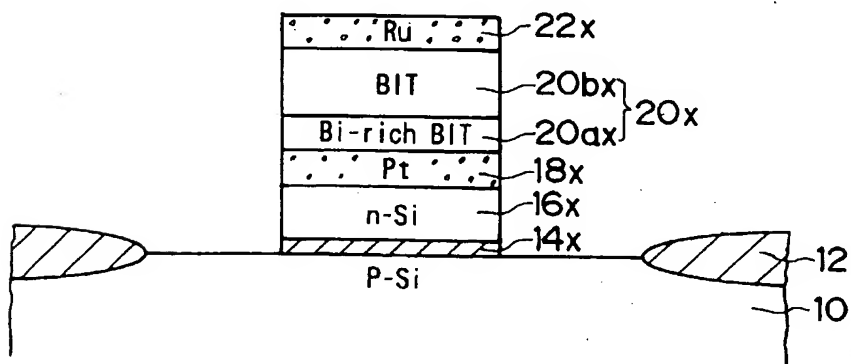


FIG. 4 (A)

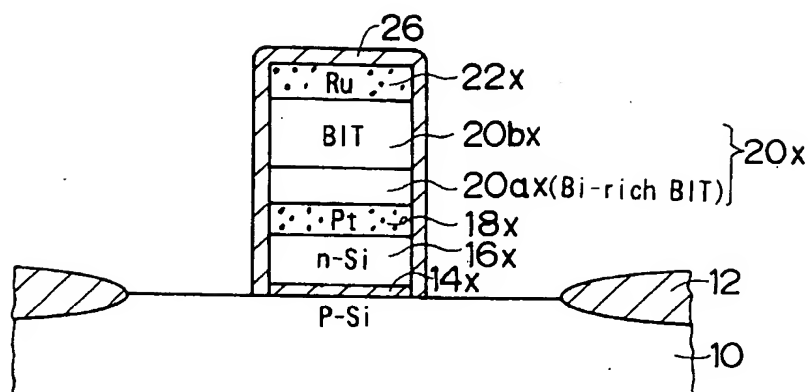


FIG. 4 (B)

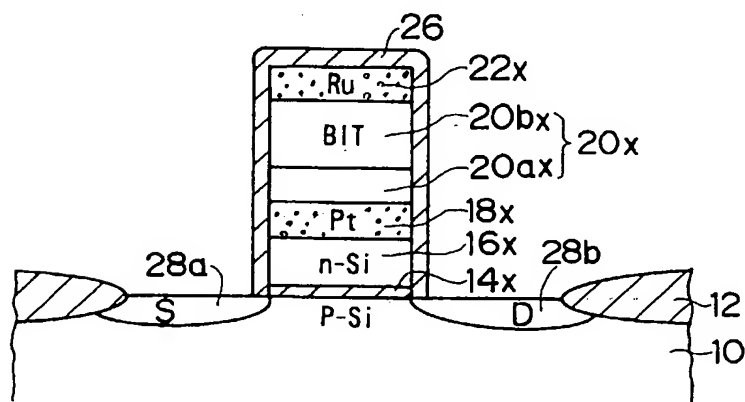


FIG. 4 (C)

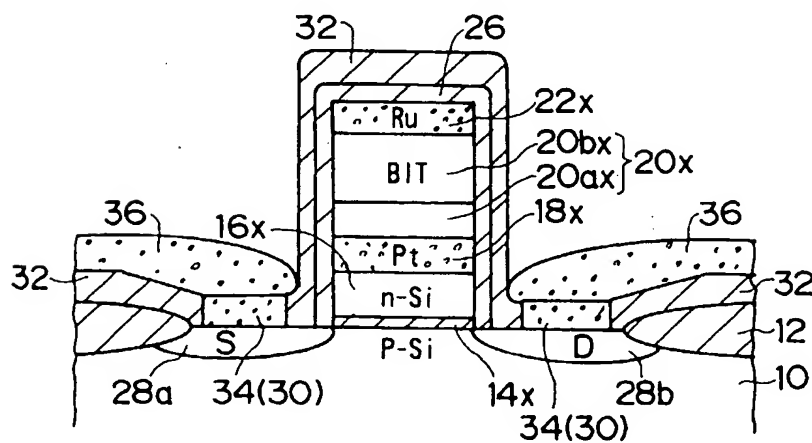


FIG. 5 (A)

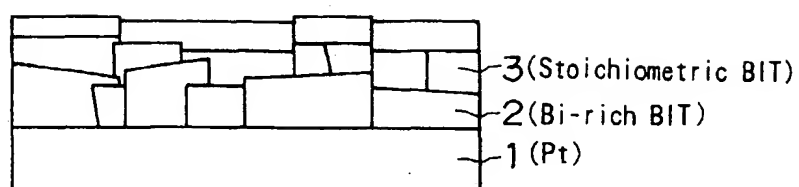


FIG. 5 (B)

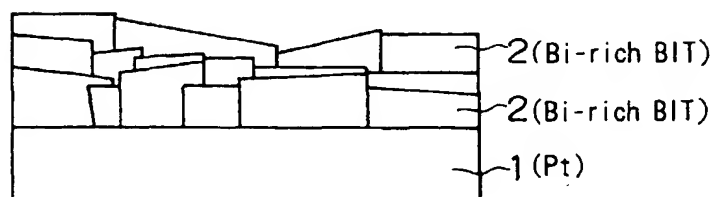


FIG. 6 (A)

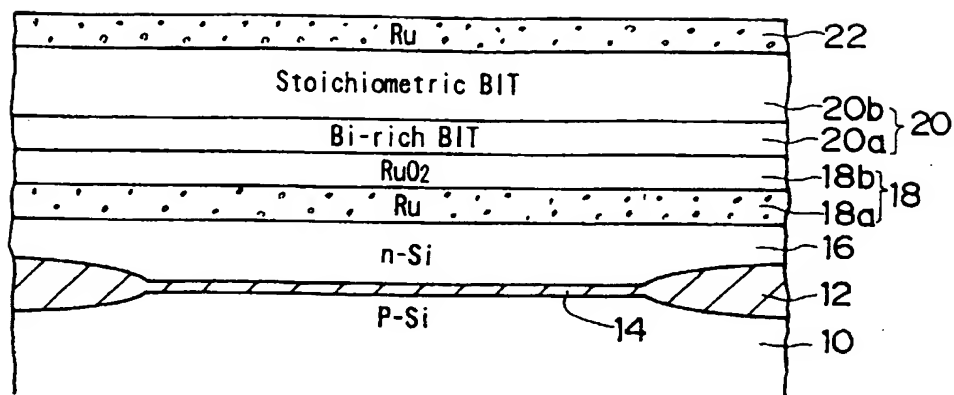


FIG. 6 (B)

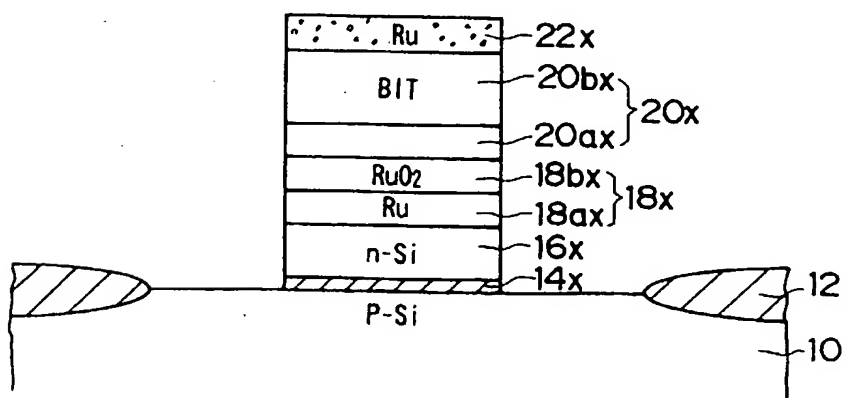


FIG. 7 (A)

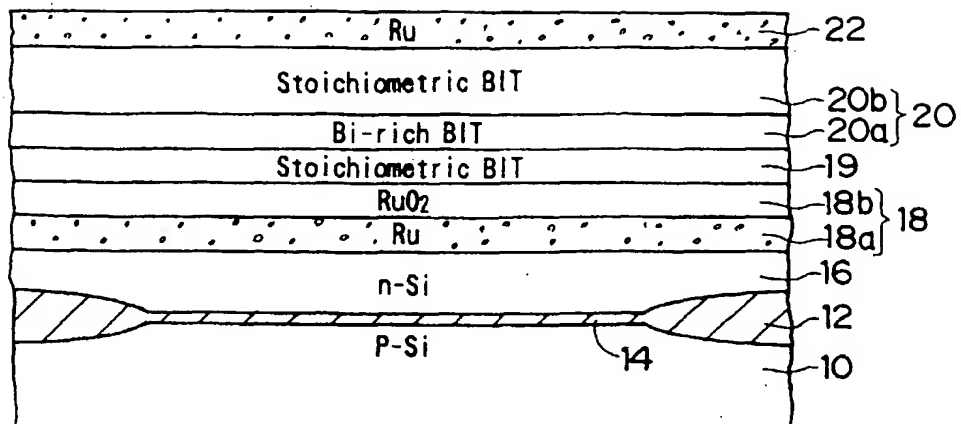


FIG. 7 (B)

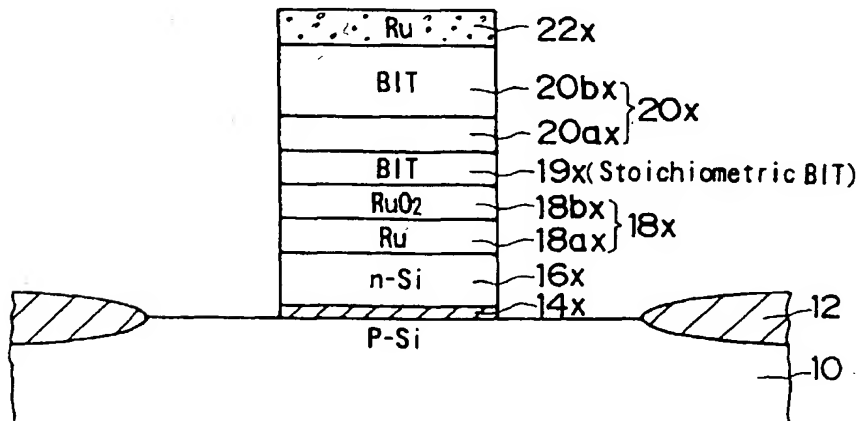


FIG. 8 (A)

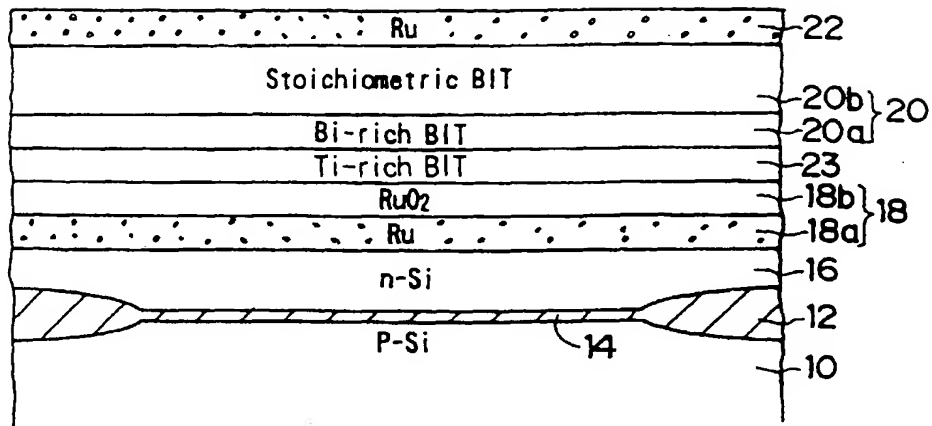


FIG. 8 (B)

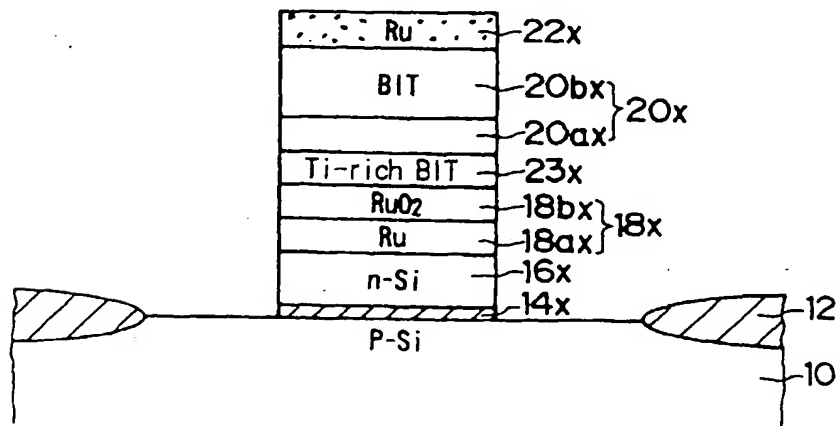


FIG. 9 (A)

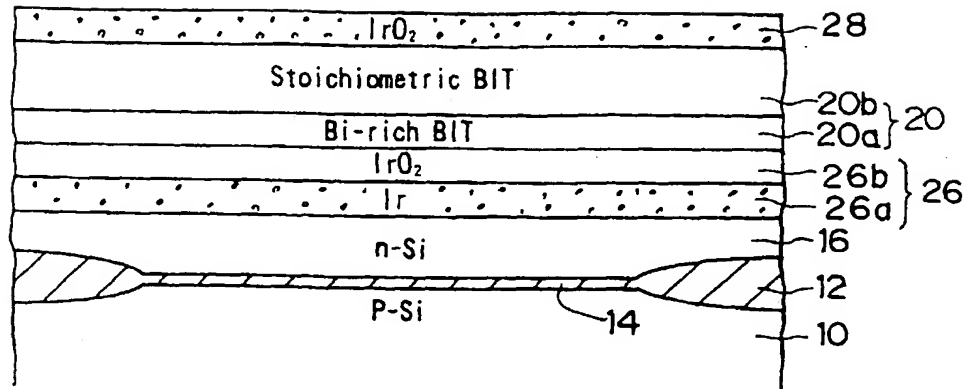


FIG. 9 (B)

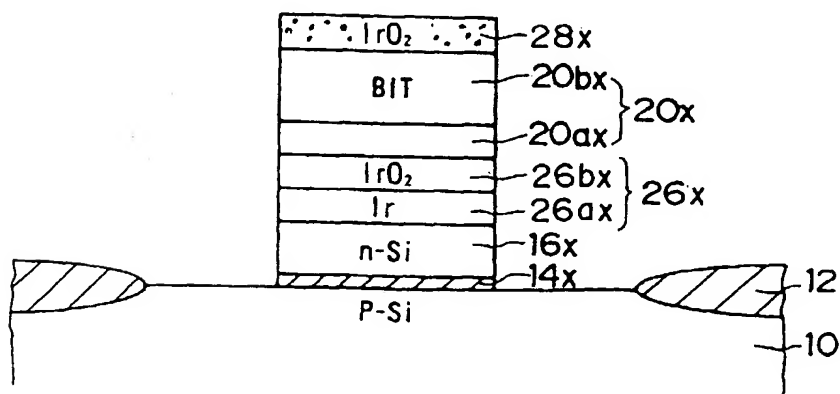


FIG. 10 (A)

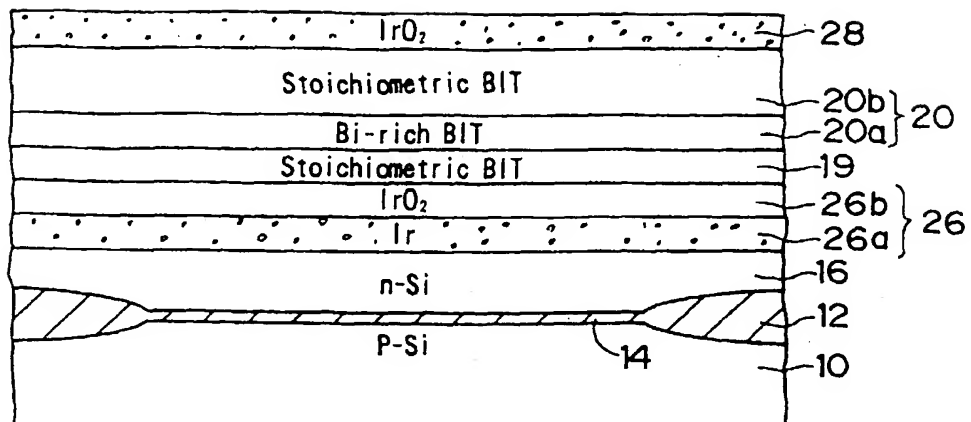


FIG. 10 (B)

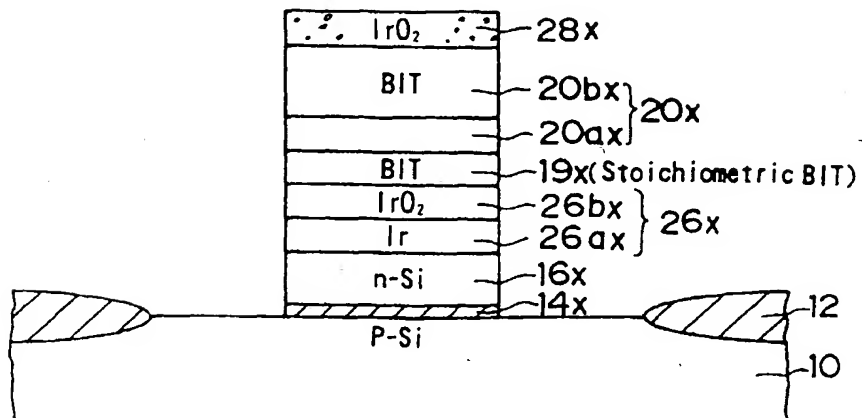


FIG. 11 (A)

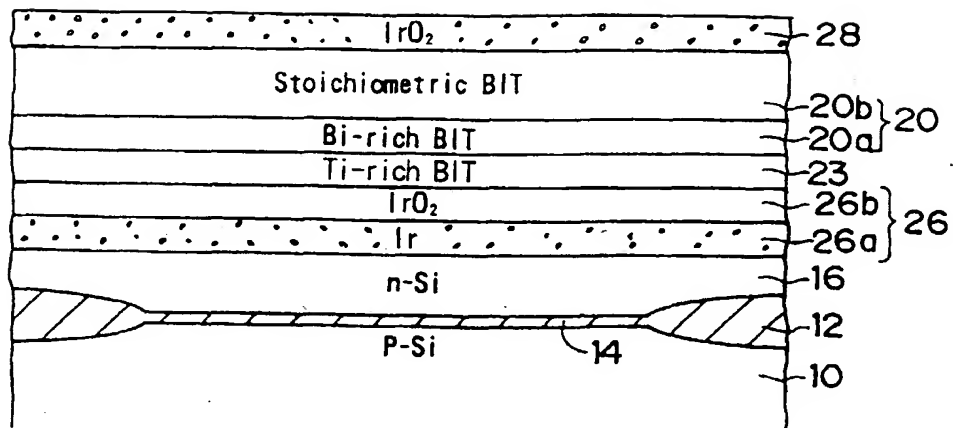
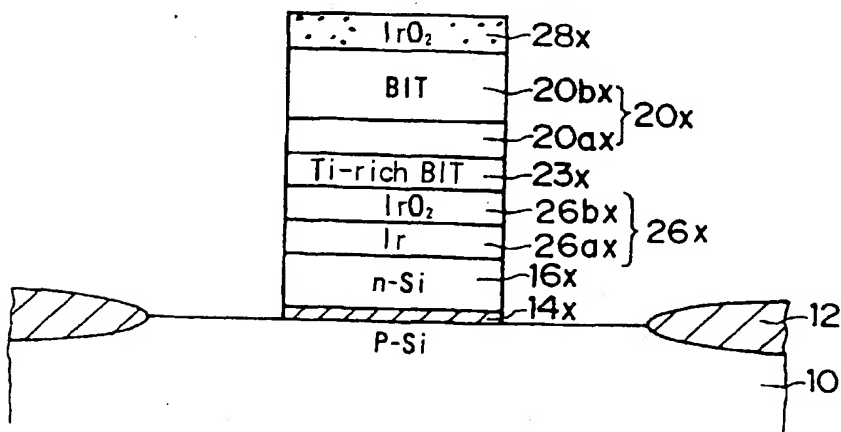


FIG. 11 (B)





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 10 8107

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	JOURNAL OF APPLIED PHYSICS, vol. 72, no. 11, 1 December 1992, pages 5517-5519, XP000323884 JOSHI P C ET AL: "RAPID THERMALLY PROCESSED FERROELECTRIC BI4TI3O12 THIN FILMS" * page 5517, column 1, paragraph 1 *	1-15	H01L27/115
A	US 5 146 299 A (LAMPE DONALD R ET AL) 8 September 1992 * column 24, line 56 - column 25, line 7 *	1-15	
A	PATENT ABSTRACTS OF JAPAN vol. 095, no. 007, 31 August 1995 & JP 07 099257 A (RICOH CO LTD), 11 April 1995, * abstract *	1-15	
A	WESCON TECHNICAL PAPERS, vol. 35, 1 November 1991, pages 390-393, XP000320562 LIDDIARD B J: "FERROELECTRIC MEMORIES: AN EMERGING TECHNOLOGY" * figure 2 *	1-15	TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01L
A	EP 0 415 750 A (NIPPON ELECTRIC CO) 6 March 1991 * claims 3,7 *	1-15	
A	IBM TECHNICAL DISCLOSURE BULLETIN, vol. 30, no. 8, 1 January 1988, page 436/437 XP000111203 "USE OF CONDUCTING OXIDES AS A DIFFUSION BARRIER IN SHALLOW JUNCTION SEMICONDUCTOR DEVICES" * the whole document *	5,9	
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 22 August 1997	Examiner Juhl, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.92 (P04C01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 10 8107

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 653 794 A (SHARP KK) 17 May 1995 * page 3, column 4, line 18 * * page 6, column 10, line 54 * -----	5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 22 August 1997	Examiner Juhl, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 01.87 (P04C01)